

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

FRENCH REPUBLIC

NATIONAL OFFICE OF INDUSTRIAL PROPERTY

PATENT OF INVENTION

XIV. - Chemical arts.

3. - EXPLOSIVE POWDERS AND MATERIALS, PYROTECHNICS.

No. 349.635

Improvements in explosives.

M. CHARLES GIRARD, residing in France.

Filed 5 April 1904.

Granted 5 April 1905. - Published 7 June 1905.

[Patent of invention whose issuance has been postponed by virtue of art. 1187 of the law of 3 July 1944, amended by the law of 7 April 1902.]

It has long been known that the combination of certain substances with a particular melting point produces a compound with melting point lower than that of the compound melting at the highest temperature.

It has been found that the combination of nitrated or azo derivatives in the proportion of their molecular weights gives rise to actual combinations whose melting point is not only lower than the melting points of the components, but also experiences a *maximum* lowering.

It should be noted in passing that the preparation of these compounds is done without difficulty. It is sufficient to bring together weighed quantities, equal to the molecular weight of each of the compounds going into the contemplated mixture, to mix them intimately, and to melt them in a water bath. The mass is then poured off. After cooling, it is ready for the desired use.

The results of experiments are presented in the following table:

Compounds | Formula | Molecular weight | Melting point | Compounds | Formula | Molecular weight
 | Melting point | Melting point of the mixture

COMPOSÉS.	FORMULE.	POIDS MOLECULAIRE.	POINT DE FUSION.	COMPOSÉS.	FORMULE.	POIDS MOLECULAIRE.	POINT DE FUSION.	POINT DE FUSION DE LA MÊME.
Azobenzol	$(C^6H^5)_2Az^2$	182	66° 5'	+ Binitrobenzine	$C^6H^4(AzO^2)^2$	168	85°	40°
				+ Binitrotoluène	$C^6H^3CH^3(AzO^2)^2$	182	71°	34° 5'
				+ Trinitrotoluène	$C^6H^2CH^3(AzO^2)^3$	227	80°	51°
				+ Trinitrocrésoline	$C^6H(OH)(AzO^2)^3$	245	175°	64°
				+ Nitronaphtaline	$C^{10}H^7AzO^2$	173	61°	37°
				+ Diauidooxobenzol	$C^6H^4AzH^2C^6H^2(AzH^2)^2$	212	117°	59°
Nitronaphtaline ..	$C^{10}H^7AzO^2$	173	61°	+ Trinitrophénol	$C^6H^3OH(AzO^2)^3$	229	122°	61°
Binitrotoluène ..	$C^6H^3CH^3(AzO^2)^2$	182	71°	+ Paronitraniline	$C^6H^4AzO^2AzH^2$	188	147°	66°
Crésylol	$C^6H^4CH^3OH$	108	31°	+ Naphtylamine	$C^{10}H^7AzH^2$	143	50°	46°
Naphtylamine ..	$C^{10}H^7AzH^2$	143	50°	+ Binitrotoluène	$C^6H^3CH^3(AzO^2)^2$	182	71°	28°
				+ Binitrobenzine	$C^6H^4(AzO^2)^2$	168	85°	40°
				+ Phénol	C^6H^5OH	94	40°	7°
				+ Paratoluidine	$C^6H^4CH^3AzH^2$	107	45°	13°

COMPOSÉS.	FORMULE.	POIDS MOLECULAIRE.	POINT DE FUSION.	COMPOSÉS.	FORMULE.	POIDS MOLECULAIRE.	POINT DE FUSION.	POINT DE FUSION DE LA MÊME.
Paratoluidine ..	$C^6H^4CH^3AzH^2$	107	45°	+ Azoxybenzide	$(C^6H^5)_2Az^2O$	198	36°	13° 5'
				+ Binitrobenzine	$C^6H^4(AzO^2)^2$	168	85°	15°
				+ Trinitrocrésol	$C^6H^3CH^3OH(AzO^2)^3$	243	107°	70°
				+ Mononitrophénol	$C^6H^4OH(AzO^2)$	139	45°	30°
				+ Binitrobenzine	$C^6H^4(AzO^2)^2$	168	85°	56°
Trinitrophénol ..	$C^6H^3OH(AzO^2)^3$	229	122°	+ Binitrotoluène	$C^6H^3CH^3(AzO^2)^2$	182	71°	47°
				+ Paronitraniline	$C^6H^4AzO^2AzH^2$	188	147°	74°
				+ Nitronaphtaline	$C^{10}H^7AzO^2$	173	61°	49°
				+ Binitronaphtaline	$C^{10}H^6(AzO^2)^2$	218	135°	80°

Any change made in these proportions causes the melting point of the mixture to rise again. For example:

Compounds	Melting point	Compounds	Melting point	Melting point of the mixture
COMPOSÉS.	POINT DE FUSION.	COMPOSÉS.	POINT DE FUSION.	POINT DE FUSION du mélange.
Binitrotoluène....	71°	1 molécule 182 gr. + Binitrobenzine....	85°	1 molécule 168 gr. # 60°
				1/2 — 84 # 47°
				1/3 — 43 # 54°
				1/5 — 33 # 56°
				1/10 — 16 # 64°
				1 — 184 # 40°
Binitrobenzine....	85°	1 molécule 168 gr. + Binitrotoluène....	71°	1/4 — 91 # 48°
				1/4 — 65 # 53°
				1/5 — 36 # 55°
				1/10 — 18 # 59°
				1 — 243 # 70°
				1/2 — 121 # 78°
				1/4 — 60 # 86°
				1/5 — 48 # 101°
				1/10 — 24 # 108°
				1 — 229 # 70°
				1/2 — 44 # 80°
				1/4 — 57 # 89°
				1/5 — 45 # 98°
				1/10 — 22 # 101°
Trinitrophenol....	107°	1 molécule 229 gr. + Trinitrocresol....	107°	
Trinitrocresol....	107°	1 molécule 243 gr. + Trinitrophenol....	132°	
Nitrocresol....	107°	—	122°	

With the help of these compounds, which play the role of fuel, one can produce remarkable explosives by combining them either with suitable supporters of combustion, such as the alkaline chlorates and perchlorates, the alkaline and ammoniated nitrates, without addition of hydrocarbons, oils, etc., or with the nitric ethers - and in particular nitroglycerin - which in the latter case makes it possible to obtain the dynamites, in which the nitroglycerin does not freeze, even at very low temperature. Furthermore, certain of the compounds whose succinct enumeration has been judiciously chosen are themselves powerful explosives, such as the mixtures of picric acid and trinitrocresylic acid, whose melting points are low enough to allow them to be poured into the shells and other hollow projectiles at the temperature of the water bath.

These types of explosives are as follows:

1) *Explosives obtained by direct mixture of the combustion supporting agent into the fuel as represented by the combination of two nitrated substances.* - Given the lowering of the melting point, it is needless to employ oil or any other material intended to give the fuel a liquid form, which is necessary for complete coating of the combustion supporting agent and which reduces the sensitivity of the mixture thanks to its fluidity. One can work at the lowest temperature desired, by judiciously selecting the compounds.

The nitrated combination is melted in the water bath in a suitable container. One adds the combustion supporting agent to it: chlorate, perchlorate or nitrate, ground into fine powder, and the mixture is triturated until perfectly homogeneous. The product thus obtained, which is very plastic at the operating temperature, is passed through a No. 20 or 30 screen, where it is granulated and forms, upon returning to normal temperature, a dry powder which can be glazed.

Various fuels can be added to these mixtures, such as: starch, sugar, metal shavings, etc.

The combustion supporting agent can also be soaked for a certain time, after having been ground to the most suitable dimensions, in one of the above-described compounds maintained in the molten state. One

obtains a very homogeneous explosive, not sweating in the temperature range as defined by the melting point of the fuel used to produce it.

As an example, the following compositions can be specified:

Potassium chlorate	7[2?] p. 100
Azobinitrotoluene (melting point 34.5°)	[2?]8
Ammonium nitrate	63
Azobinitrotoluene	37
Ammonium perchlorate	69
Azobinitrotoluene	31
Potassium chlorate	79
Azodiamidoazobenzene (melting point 59°)	21
Potassium chlorate	65
Picroazobenzene (melting point 61°)	35
Potassium chlorate	76
Azoparanitraniline (melting point 66°)	24

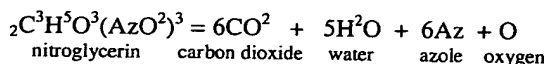
These proportions are calculated to obtain carbon dioxide and water as the final products, but they could be modified, of course, to achieve a more or less complete combustion, depending on the desired force of the explosive and its conditions of use; they will thus allow one to obtain a full range of explosives, from the most powerful ones, with elevated temperature of detonation, down to the fire damp kind.

2) *Explosives obtained by adding combinations of nitrated substances to the nitric ethers and especially to nitroglycerin.* - It is known that the presence of foreign substances added in minimal quantity to nitroglycerin has the effect of retarding or preventing its freezing. The use of certain solid nitrated derivatives of the aromatic series of carbides has been indicated elsewhere and quite recently for this purpose.

The advantage and the novelty of the use of the combinations described above lies in the possibility of dissolving these combinations in the nitric ether at the lowest possible temperature, which eliminates any danger and which could not have been done with the substances mentioned above, given the fact that the most fusible of them melts around 59°.

One can thus dissolve in the nitroglycerin the combinations of azobenzene and its homologues, which would be dangerous to do with azobenzene alone, which melts at 66.5°. Now, this latter substance has the property, which it shares with certain azo compounds, of considerably lowering the freezing point of nitroglycerin. Furthermore, azobenzene is a neutral substance which cannot bring about alteration or decomposition of nitroglycerin, which is always to be feared with certain nitrated derivatives that are very often more or less acid, and finally it imparts a remarkable insensitivity to the dynamites in which it is contained.

The methodical addition of the above-described compounds to dynamites gives them an augmented power. In fact, it is known that nitroglycerin contains an excess of oxygen, which is released at the instant of its detonation, as represented by the following equation:



Now, the free oxygen can burn the carbon and the hydrogen contained in the compounds added to the nitric ether, and the formation of the gases resulting from this reaction increases the power of the explosive.

The proportion of the nitrated compounds to be added to nitroglycerin in order to obtain all of these advantages is approximately 5%.

The preparation of dynamite with the help of this process merely involves dissolving the combination in nitroglycerin at its melting point, then bringing about gelatinization or adding kieselguhr, as usual.

All that has been said above applies to the nitric ethers of the aliphatic series.

If one wishes to prepare smokeless powders, one dissolves the nitrocellulose or mixtures of nitrocellulose in a suitable solvent, maintaining the desired quantity of the chosen combination in solution.

3) *Explosives especially useful for loading of hollow projectiles (shells, torpedoes, etc.).* - Shells intended for destruction of artillery depots, military works, monuments, etc., are generally loaded at present with either melted picric acid or trinitrocresol.

To load the shells, which should be warmed in order to prevent excessively rapid crystallization, the filling substance is brought up to its melting point in a bath of calcium chloride, that is, 122° for picric acid and 107-108° for trinitrocresol.

Without claiming that the two nitrated substances can undergo alteration under the conditions in which they are generally melted, one should nevertheless point out that it is always desirable, from the standpoint of safety, to heat the nitrated substances as little as possible, whatever they are.

Now, with the mixture in terms of molecular weights, the melting point is reduced to 70°.

The two substances in powder form are intimately mixed and melted in the water bath.

Thus, one will always be below the melting point of the two compounds, that is, in the best possible conditions from the standpoint of safety.

SUMMARY.

1) The explosives which belong to the first category, obtained with the compounds indicated in the enclosed table, or those which can be obtained from the information provided, combined with combustion supporting agents such as alkaline chlorates and perchlorates, alkaline or ammoniated nitrates, and whose combination can be done without danger and very intimately in the absence of oils, hydrocarbons, etc., thanks to the lowering of the melting point of the compounds which play the role of fuel in the explosive, and the manufacturing processes making it possible to obtain them.

2) The explosives obtained by combining the nitric ethers with any of the compounds indicated above or those which can be prepared with the help of the information provided and which make it possible to obtain, in particular, dynamites which do not freeze, having an assured preservation and a considerable increase in power, as well as the methods by means of which one obtains these explosives.

3) The powerful explosives in themselves, such as the mixtures of picric and trinitrocresylic acid, the methods for obtaining them, and the application of these explosives to the loading of hollow projectiles (shells, torpedoes, etc.).

C. GIRARD

Attorney:

Ch. THIRION and J. BONNET